



A reversible water electrolyser with porous PTFE based OH[−] conductive membrane as energy storage cells



Xu Wu^{a,b,*}, Keith Scott^{a,*}, Fang Xie^b, Neil Alford^b

^aSchool of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom

^bDepartment of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

HIGHLIGHTS

- A reversible water electrolyser was prepared with porous PTFE based OH[−] membrane.
- Current density was improved by adopting the PTFE composite OH[−] membrane.
- The peak power density in fuel cell mode achieved 0.163 W cm^{−2} at 45 °C.
- In the water electrolyser mode, degradation rate was only 0.0379 mV h^{−1}.

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ABSTRACT

An OH[−] conductive anion exchange membrane was prepared by a pore-filling method with porous polytetrafluoroethylene and a quaternary ammonium polymethacrylate ionomer. The composite membrane exhibited less swelling ratios of thickness and area variation and stronger tensile strength than the pristine polymethacrylate membrane. The ionic conductivity of the composite membrane was not as good as the pristine polymethacrylate ionomer membrane. However, the composite membrane was ultra-thin therefore it led to a smaller ionic resistance of the MEA and improved current densities. In fuel cell mode, the peak power densities were respectively 0.114 and 0.163 W cm^{−2} at 20 and 45 °C. In water electrolyser mode, at a current density of 100 mA cm^{−2} the cell voltages were about 1.61 V and 1.52 V respectively at 22 °C and 50 °C. In the water electrolyser mode, the degradation rate was only 0.0379 mV h^{−1} after 120 h at a current density of 100 mA cm^{−2} at 22 °C.

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1. Introduction

Electrochemical energy storage cells are essential devices for national grid and renewable power sources such as solar and wind energy, of which the power is usually generated in the form of electricity [1]. Water electrolyser is one of the promising candidate devices for storing electricity into chemical energy, with H₂ as the energy carrier [2]. The H₂ gas produced by electrolyzers can be collected and consumed as fuels when required. Or in a more efficient way, the energy carried by H₂ gas can be released to electricity by fuel cells [3]. The combination of water electrolyzers and fuel cells is often called regenerative fuel cells (RFC), which can be considered more advanced than conventional secondary batteries [4]. If a water electrolyser can also work as a fuel cell once H₂ and O₂ are supplied

back to corresponding electrodes, it is often called a unitized regenerative fuel cell (URFC) [5–10]. Such devices may also be called reversible water electrolyzers (RWE), since they exhibit both function of storing electricity into chemical energy as electrolyzers and then release chemical energy back to electricity with the reversed electrochemical process. The RWE can work in two function modes: the fuel cell mode and the water electrolyser mode. In the water electrolyser mode, electric energy will be stored into chemical energy via electrolysis of water to form H₂ and O₂. While in the fuel cell mode, this device can generate electricity when required, with H₂ and O₂ supplied back to each electrode with producing water. There are considerable works on developing the URFC in past three decades [5–10]. However, most URFC are based on cationic perfluorosulfonic acid (PFSA) ionomers, in which expensive noble metal catalysts and corrosion resistant materials are necessary for good stability and cycle life [5–10]. For example in the bifunctional oxygen electrode, the catalysts are often based on expensive Pt with IrO₂ [8]. It is of increasing interests to employ anionic OH[−] conductive polymer electrolyte membranes for regenerative fuel cells, in which case

* Corresponding authors. Department of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom. Tel.: +44 191 2228771; fax: +44 191 2225292.

E-mail addresses: xu.wu@imperial.ac.uk, xu.wu.newcastle@gmail.com (X. Wu), k.scott@ncl.ac.uk (K. Scott).

non-precious-metal catalysts can be adopted in the electrodes [11]. The configuration of the RWE in our study is schematically illustrated in Fig. 1. The OH^- conductive membrane is the core component of RWE, as shown in Fig. 1. A significant advantage of using OH^- conductive polymer electrolyte instead of KOH electrolyte is that only deionised water is required for the water RWE system [11]. The catalyst layers for hydrogen and oxygen electrodes are respectively attached to opposite sides of the membrane as close as possible to reduce electrolytic resistances. Usually, the porous current collectors are attached to the catalyst layers to form the membrane electrode assembly (MEA). The current density performances as well as stability of the RWE system would often mainly depend on the parameters and methods of MEA preparation. As shown in Fig. 1, the oxygen side often exhibits highly corrosive environment especially when anodic oxygen evolution reaction happens. Therefore in our design a gold coated titanium mesh was employed as the current collector for the oxygen electrode. It can be seen from our previous report [11] that the current densities of RWE are several times smaller than that of typical URFC. Therefore to improve the current densities, we have been working on improving the electrochemical activity of electrodes and reducing the total resistance of the electrolytic cell.

Previously, we developed a quaternary ammonium Poly(DMAEMA-co-TFEMA-co-BMA) ionomer (qPDTB- OH^-) for the alkaline membrane cells [12]. However, the qPDTB- OH^- ionomer was only utilized as the binder for catalyst layers in the previous study, the qPDTB- OH^- membrane exhibited remarkable swelling effects when immersed in water for a long time. Then in this study, an ultra-thin composite membrane of qPDTB- OH^- ionomer was prepared by filling the pores of a porous polytetrafluoroethylene (PTFE) with qPDTB- OH^- . The preparation method of composite membranes with polymer electrolyte and porous PTFE was developed earlier for high temperature proton exchange membranes fuel cells [13]. Yamaguchi [18] originally proposed the concept of pore-filling membranes for polymer electrolyte fuel cells. Porous or expanded PTFE were adopted in some pore-filling composite membranes of PFSA ionomers [19–21]. Composite membranes of porous PTFE and quaternary ammonium polymer were reported recently for alkaline anion exchange membrane fuel cells [14,26]. In this study, the pristine qPDTB- OH^- membrane and the

composite membrane were compared in terms of conductivity, tensile strength, and the swelling effect. This membrane was applied in a practical single-cell reversible water electrolyser and the current density performances were evaluated in both fuel cell mode and water electrolyser mode. The stability of the MEA with this composite membrane was evaluated by continuous operation for several days.

2. Experimental methods

2.1. Membrane preparation

The porous PTFE membrane adopted in this work was obtained from Membrane Solution Ltd (United States of America). The thickness of this porous PTFE was 25 μm and had a porosity of 82% and pore size of 0.3–0.6 μm . The qPDTB- OH^- ionomer was prepared according to a published method [12]. The hydrophobic PTFE sheet was pre-treated for better impregnation of qPDTB, using the method developed by Scott and Li [13]. Firstly, the porous PTFE was treated with seven parts H_2SO_4 (98 wt% aqueous solution, Aldrich) and three parts H_2O_2 (30 wt% aqueous solution, Aldrich) at 80 $^\circ\text{C}$ for 1 h. Following this, the porous PTFE was rinsed with copious amounts of de-ionised (DI) water and further treated by immersion in a solution containing one part aqueous NaOH (1.0 mol dm^{-3}) solution, one part H_2O_2 (30 wt% aqueous solution), and five parts DI water at 70 $^\circ\text{C}$ for 30 min, followed by rinsing with copious amounts of DI water. Then PTFE sheet was pre-treated in boiling ethanol for 30 min. Then it was immersed in 5 wt% qPDTB alcohol solution for 20 min with ultrasonication, and then casted and dried at room temperature for 40 min to complete impregnation. The impregnation process was repeated several times to achieve expected weight. This composite membrane was changed from halide form to OH^- form by immersing in a 0.5 mol dm^{-3} KOH solution for several hours and then rinsed with deionised water several times until rinsing water pH ≈ 7 .

2.2. Membrane characterization

Morphology of the membrane samples was studied by scanning electron microscopy (SEM, JEOL JSM5300LV). Ionic conductivity of

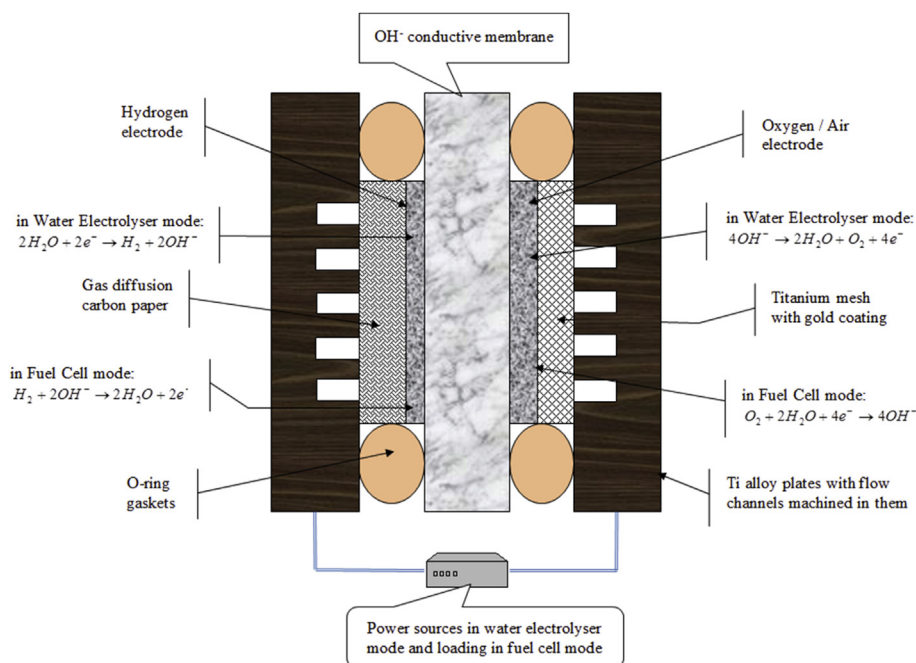


Fig. 1. Schematic figure of reversible water electrolyser with OH^- conductive membranes.

the membranes in OH^- form was determined by four point AC impedance method, as described elsewhere [15]. Relative humidity was controlled with a N_2 purging humidifier and was monitored by a temperature–humidity sensor (Vaisala HMT360) of which the probe was installed inside the conductivity measurement fixture. Ion exchange capacity (IEC) of the membrane was measured by acid–base back titration [16]. Tensile strength was tested with an Instron 4505 tensile machine. The water content of the membrane (λ) was defined as average number of water molecules per the conducting functional site, by the following equation:

$$\lambda = \frac{(W_h - W_d)/W_d}{\text{IEC} \times M_w}$$

where IEC is the ion exchange capacity (i.e. OH^- ion content per gram of membrane), W_h and W_d are respectively the weight of the membrane in dry form and after hydration, M_w is the molecular weight of water, 18 g mol^{-1} . The swelling ratio of thickness (H_T , %) was defined by the following equation:

$$H_T = \frac{\delta_h}{\delta_d} \times 100$$

where δ_d and δ_h are respectively the membrane thicknesses in dry form and after hydration. To measure the swelling effects, the membrane in OH^- form was firstly immersed in room temperature deionized water for 10 days and then the thickness variations were gradually measured when drying the swollen membrane from fully hydrated to totally dry.

2.3. Membrane electrode assembly preparation and measurement

The $\text{Cu}_{0.6}\text{Mn}_{0.3}\text{Co}_{2.1}\text{O}_4$ nanometre powder was adopted as catalyst for the bifunctional oxygen electrode [11]. This $\text{Cu}_{0.6}\text{Mn}_{0.3}\text{Co}_{2.1}\text{O}_4$ catalyst was prepared according to previously published method [17]. The MEA was prepared by catalyst coated on membrane method with the qPDTB- OH^- ionomer as binder for catalyst layers, according to published procedures [11]. In this study, 20 wt% Pt/C (Alfa Aesar) was adopted in the hydrogen electrode with a loading of 0.1 mgPt cm^{-2} . To improve the stability of the MEA, a cross-linker was added to qPDTB for preparing catalyst inks. MEA was formed by hot-pressing porous current collectors onto the catalysts coated membrane. The MEA was immersed in deionised water for at least 24 h before polarisation tests. When the MEA was installed in the testing system as shown in Fig. 1, the oxygen electrode was connected to a potentiostat (ACM 946) as working electrode and the hydrogen electrode side was adopted as both reference and counter electrode. The polarization curves of the practical MEA were obtained with a scan rate of 5 mV s^{-1} . Stability of electrolyser mode was analyzed by chronopotentiometry at a constant current density of 100 mA cm^{-2} for several days.

3. Results and discussion

3.1. Membrane preparation

It can be seen in the SEM images in Fig. 2 that the as received PTFE membrane is highly porous. With the qPDTB ionomer impregnated into the pores of the matrix, the membrane became non-porous. The impregnation process was repeated several times to ensure that the pores of the PTFE are fully filled with qPDTB. Table 1 lists the variation of the weight of a sample membrane after each impregnation treatment. After the treatment with qPDTB solution, the membrane was dried to evaporate the alcohol solvent

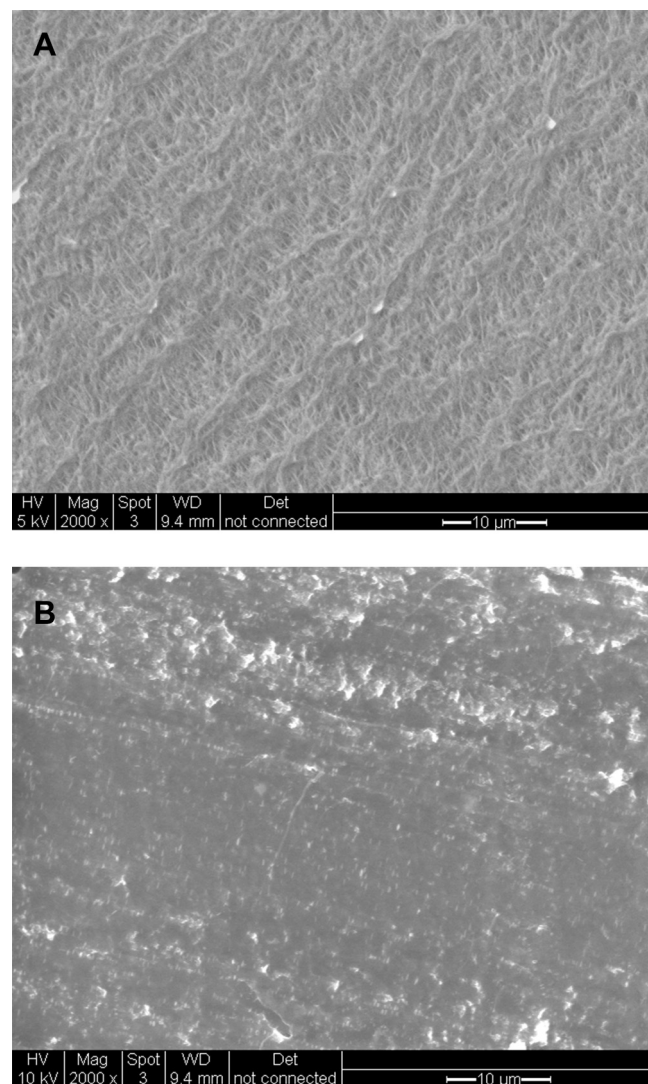


Fig. 2. Morphology of (A) porous PTFE membrane and (B) PTFE + qPDTB composite membrane.

letting qPDTB ionomer to fill the pores. However, with only one treatment the qPDTB ionomer could have filled only parts of the volume of the pores inside the porous PTFE membrane. Then the repetitive impregnation processes were adopted in this study. Then the filler qPDTB ionomer gradually filled all the rest volumes of the pores and eventually spilled to the surface of the composite membrane. Considering the porosity of this porous PTFE membrane is about 0.82, and the density of PTFE and qPDTB are respectively about 2.2 and 1.2 g cm^{-3} , it can be estimated that when the weight of this sample membrane (originally 12.5 mg) increases to 43.6 mg , the pores would ideally be fully filled by qPDTB and little qPDTB is outside the surface of PTFE. As seen in Table 1, after 5 impregnation processes, the weight of membrane increased from

Table 1

Weight of a PTFE + qPDTB membrane sample after repetitive impregnation treatments.

Original weight	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5
12.5 mg	18.9 mg	25.1 mg	31.4 mg	37.9 mg	44.5 mg

12.5 mg to 44.5 mg. In this study, all composite membrane samples were prepared by 5 times impregnation treatments.

3.2. Membrane properties

3.2.1. Water uptake and swelling effects

The ion exchange capacities (IEC) of pristine qPDTB-OH⁻ membrane and PTFE + qPDTB-OH⁻ membrane were determined by acid–base back titration method and the values were respectively 1.32 ± 0.04 and 1.02 ± 0.05 meq g⁻¹. Apparently, the PTFE part of the composite membrane does not contain any quaternary ammonium function groups, therefore when the weight of PTFE was included the IEC of the composite was smaller than the pristine ionomer [18]. Fig. 3 compares the influences of water content (λ) on the swelling ratios. As shown in Fig. 3A and B, after immersing the membranes in deionised water for about seven days there was hardly any further increase in the water contents. The effect of water swelling on this polymethacrylate based quaternary ammonium ionomer is excessive, compared with PFSA ionomer membranes [18]. For example in Fig. 3C when λ was about 100, the H_T of qPDTB-OH⁻ was about 185%. The swelling effects may not only lead to larger ionic resistance of the membrane, but may also cause some problems of the MEA such as stability [19]. However, it can be noticed that the swelling ratios of the PTFE reinforced composite membrane are much smaller than the pristine ionomer. The maximum thickness swelling ratio H_T of PTFE + qPDTB-OH⁻ was about 146%.

3.2.2. Conductivity

The ionic conductivity of porous PTFE based composite membranes was usually not as good as the filler ionomer [18–21]. In this study, the decrease of conductivity was also observed when the qPDTB ionomer was made into composite membranes with porous PTFE. This difference in conductivity may possibly be due to the

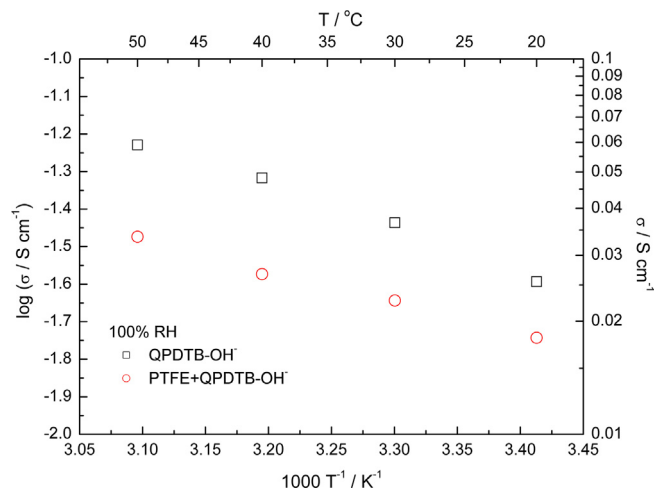


Fig. 4. Conductivity of qPDTB-OH⁻ and PTFE + qPDTB-OH⁻ membranes.

differences in IEC and water content. However as the porosity is 82% then by a Bruggeman relationship the PTFE based membrane could have a factor of $0.82^{1.5} = 0.74$ lower conductivity than the pure ionomer membrane. This value is in broad agreement with the ratios of conductivities of the pristine and PTFE membrane. As shown in Fig. 4, the conductivity of PTFE + qPDTB-OH⁻ membrane with relative humidity around 100% increased from about 0.018 S cm^{-1} to 0.034 S cm^{-1} when temperature increased from 20 °C to 50 °C. Besides, water transport properties are interesting factors in the alkaline anion exchange membranes [22] and the incorporation of PTFE may have some impacts on that point. However, there are rare data on the water transport properties of porous PTFE based OH⁻ membranes in literature. According to a simple model of water electrolyzers [23], area specific resistance of

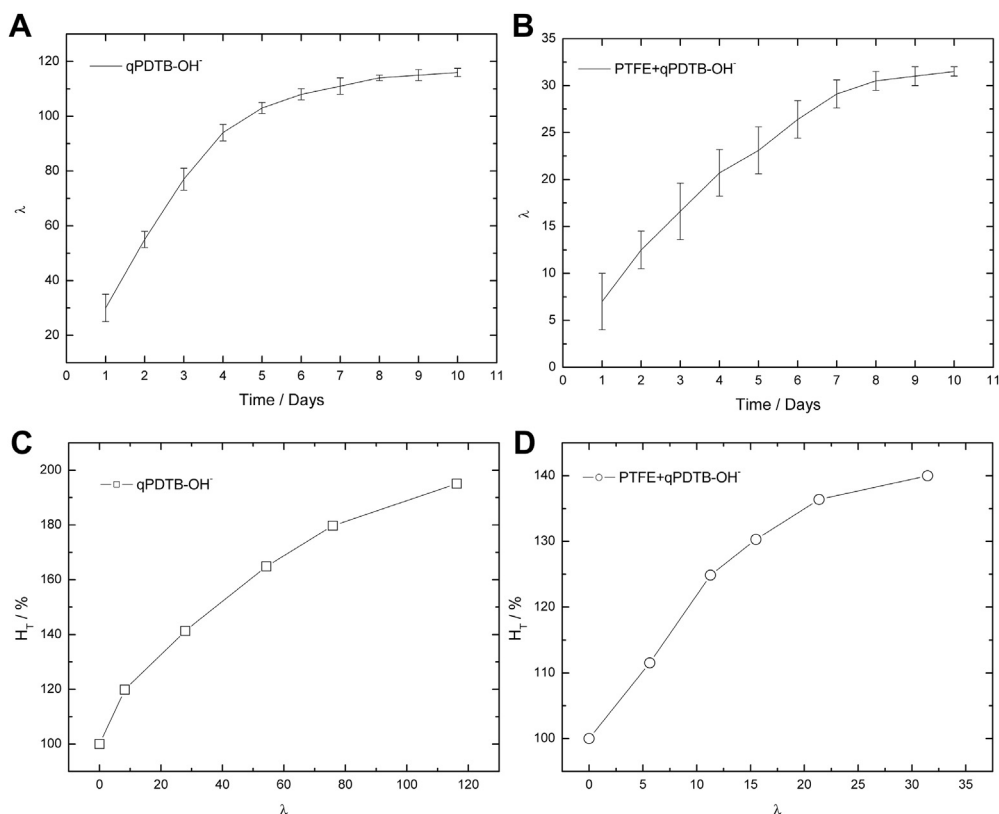


Fig. 3. Water content vs. immersing time and swelling ratio vs. water content of qPDTB-OH⁻ and PTFE + qPDTB-OH⁻ membranes.

the MEA is an important factor of improving current density performances. The area specific resistances of the pristine qPDTB-OH[−] membrane (about 200 μm) and the PTFE + qPDTB-OH[−] composite membrane (about 30 μm) were respectively c.a. $0.784 \Omega \text{ cm}^2$ and $0.167 \Omega \text{ cm}^2$ at 20 °C. The resistance of PTFE + qPDTB-OH[−] composite membrane was much smaller, which is because the composite membrane is ultrathin although its conductivity was not as good as the pristine ionomer.

3.2.3. Tensile strength

The stress strain curve of PTFE + qPDTB-OH[−] is shown in Fig. 5, from which the Young's modulus and tensile strength could be determined. The Young's modulus of the PTFE + qPDTB-OH[−] membrane was about 0.406 GPa, which is better than the qPDTB-OH[−] membrane [12]. The tensile strength was also improved by incorporating the porous PTFE in the membrane, which was greater than 10 MPa. Good mechanic properties are necessary for these OH[−] conductive membranes because the membranes will be applied in the RWE with compression to ensure good sealing of water and gas. The enhanced Young's modulus and tensile strength may indicate good stability and reliability of the PTFE + qPDTB-OH[−] membrane.

3.3. Current density performances

The current density performances in both fuel cell mode and water electrolyser mode are shown in Fig. 6. The open circuit voltage in fuel cell mode was about 1050 mV, which corresponds to the good ORR catalytic activity of the $\text{Cu}_{0.6}\text{Mn}_{0.3}\text{Co}_{2.1}\text{O}_4$ electrode [11] and also indicates little gas crossover of the MEA. Crossover of H_2 gas to the oxygen electrode is often a problem in H_2 fuel cells, which may lead lowering of the OCV by several hundred mV and may reduce the stability of the MEA. The composite membrane in this study is based on a highly porous PTFE sheet therefore it is important to carefully fill all the pores with qPDTB to ensure good restriction of gas crossover.

The activation loss (exponential range of polarization curves) was considerable in the fuel cell mode, as shown from the rapid decrease of current density from 1000 mV to 650 mV. The fuel cell mode polarisation curve turned to IR control from voltage was below about 650 mV. Although the content and composition of oxygen electrode was already optimized regarding the water electrolyser mode, apparently it is necessary to further improve the electrode with respect to oxygen reduction. It can be seen that

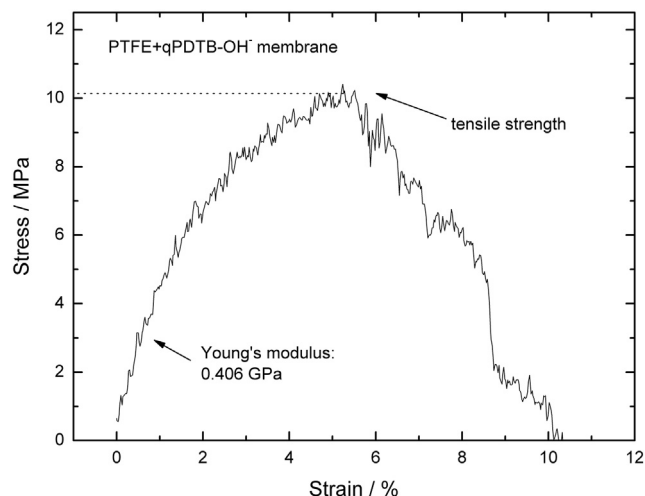


Fig. 5. Stress strain curve of PTFE + qPDTB-OH[−] membrane.

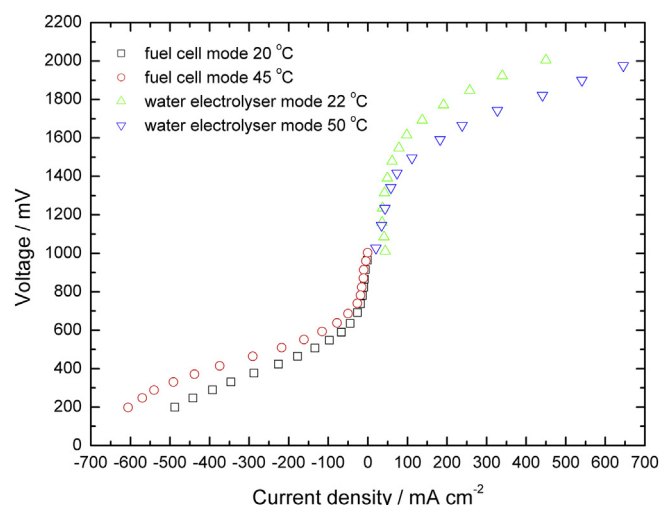


Fig. 6. Polarisation curves in fuel cell mode and water electrolyser mode.

(from 0 to -100 mA cm^{-2}) when the temperature was increased from 20 °C to 45 °C the activation overpotential fell. The apparent electrolytic resistance of the MEA can be estimated from the ohmic loss region of the polarization curves, of which the values are respectively about $1.5 \Omega \text{ cm}^2$ at 20 °C and $1.2 \Omega \text{ cm}^2$ at 45 °C. Increasing temperature both improved the kinetics of electrochemical reactions and the ionic conduction. The peak power densities at 20 °C and 45 °C were respectively 114 and 163 mW cm^{-2} . The peak power density obtained in this study is comparable with results obtained with commercial Pt/C electrode [14]. However, such power density performances are several times smaller than that of PEMFC, of which the typical peak power density is $0.5\text{--}0.8 \text{ W cm}^{-2}$ [13].

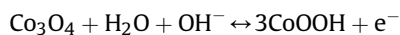
On the other hand, the overpotential in water electrolyser mode was less than that in fuel cell mode. For example at 50 °C the polarisation curve became IR control after the voltage increased above about 1500 mV. It could also be observed that when temperature increased from 22 °C to 50 °C the activation loss (as shown in $0\text{--}150 \text{ mA cm}^{-2}$) decreased. Meanwhile, the apparent MEA resistance decreased from about $0.896 \pm 0.061 \Omega \text{ cm}^2$ at 22 °C to $0.737 \pm 0.010 \Omega \text{ cm}^2$ at 50 °C. The current density performance in water electrolyser mode is better than previous results with radiation grafted membranes [12], which can be attributed to the smaller resistance of the membrane as discussed in Section 3.2.2. However, the current densities of water electrolyzers with OH[−] membranes are still not as good as that of PEMWE, of which the current density was usually around 1 A cm^{-2} with a voltage around 1.6–1.7 V [15,24].

The gap between the currents of the PEM system and OH[−] membrane system in both fuel cell mode and water electrolyser mode may be narrowed by increasing the operation temperature or by making larger electrode areas of RWEs with OH[−] membranes. Increasing operational temperature may enhance the electrode reactions and improve ionic conductivity. However it might also result in faster degradation of quaternary ammonium functional groups [25]. Increasing electrode area is practical because the material costs of RWE with OH[−] membranes are much cheaper than regenerative fuel cells based on PFSA membranes, especially with cheap non-precious-metal catalysts [12]. Besides, as energy storage cells the RWE will in most cases be stationary, so there is less concern about the volume of the system. Another important parameter for evaluating RWE is the efficiency of energy storage. The fuel cell to electrolyser voltage ratio at a current density of 100 mA cm^{-2} achieved c.a. 34% at 22 °C. This value is better than

31.9% in our previous publication [11], which is because of enhanced current density performances in both fuel cell mode and water electrolyser mode with the PTFE + qPDTB-OH⁻ membrane.

3.4. Water electrolyser mode stability

Stability of fuel cells and water electrolyzers is of vital significance in terms of practical applications for years. For the reversible water electrolyzers, the stability in electrolyser mode may be more critical than in fuel cell mode, because that the high voltage at anode may facilitate degradation of components, such as corrosion of current collectors, oxidation of ionomers, and degradation of quaternary ammonium function groups. Therefore, a relatively low voltage (e.g. below 2 V) is preferable for water electrolyzers although increasing voltage may increase the current density, i.e. H₂ production rate. Fig. 7 shows a typical short term stability test by chronopotentiometry at a constant current density of 100 mA cm⁻² for several days. The voltage in Fig. 7 increased slightly in the first 60 h and then became stable around 1.75 V. Some small peaks and valleys could be observed in the first 120 h of the curve in Fig. 6, which might be due to the influences of randomly generated gas bubbles. Degradation rate after 120 h was only 0.0379 mV h⁻¹, indicating that the MEA would be stable in continuous operation for several thousands of hours. Polarisation curves before and after stability test of Fig. 7 were determined and demonstrated in Fig. 8. It can be obtained from Fig. 8 that the apparent MEA resistances before and after stability test were respectively $0.896 \pm 0.061 \Omega \text{ cm}^2$ and $0.902 \pm 0.048 \Omega \text{ cm}^2$, which means that there were hardly any degradations of the ionomers during the stability test. Besides, the two plots in Fig. 8 exhibited almost identical IR corrected voltages of water electrolysis before and after stability test. This infers that the current density difference between the two curves in Fig. 8 was probably mainly due to changes of the catalyst surface. In previous studies [17], some considerable current could be observed on the cobalt oxide electrode due to the following reaction:



After the stability test the current attributes to this surface reaction would have declined, which corresponds to the current density differences between the two curves in Fig. 8 and could also explain the voltage variation in the first 60 h of stability test.

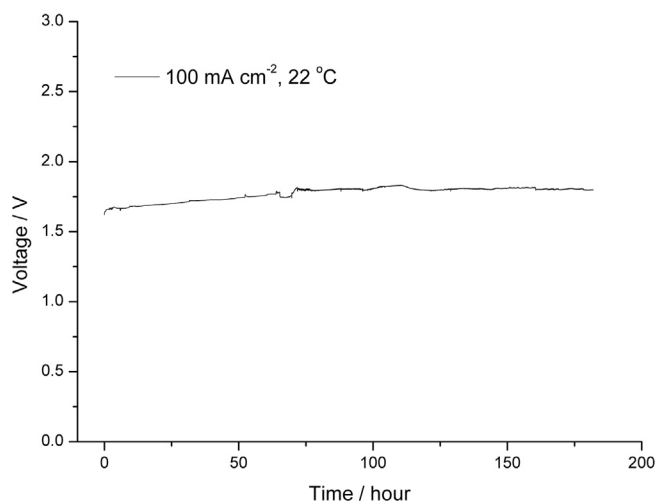


Fig. 7. Short term stability test at 22 °C and with a constant current density of 100 mA cm⁻².

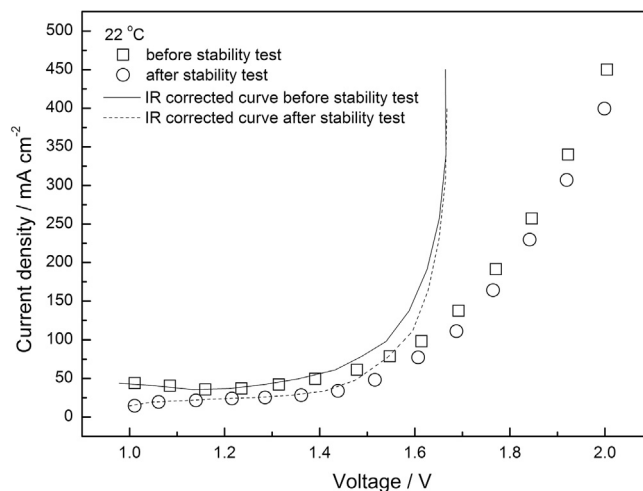


Fig. 8. Polarisation curves before and after the stability test of Fig. 7.

4. Conclusions

A reversible water electrolyser was prepared with an advanced OH⁻ conductive membrane based on porous PTFE. The PTFE + qPDTB-OH⁻ composite membrane exhibited better swelling effects and mechanical strength than the pristine qPDTB-OH⁻ membrane. The ionic conductivity of PTFE + qPDTB-OH⁻ membrane was not as good as the qPDTB-OH⁻ membrane. However, due to this PTFE + qPDTB-OH⁻ membrane could be ultra-thin (30 μm), the resistance of the membrane was reduced and current densities were improved compared with previous results. In the fuel cell mode, the peak power density achieved 163 mW cm⁻² at 45 °C. In water electrolyser mode at a current density of 100 mA cm⁻² the voltage was only 1.61 V at 22 °C. In future works, the water transport properties is of interests with the influences of PTFE in the composite. The current density in both fuel cell mode and water electrolyser mode shall be further improved by further reducing ionic resistance and improving electrode parameters. This reversible water electrolyser operated with only deionised water, which is unique compared with KOH based fuel cell and water electrolyser systems. Besides, a non-precious-metal oxygen electrode was adopted in this study, which is much cheaper than the Pt-Ir based oxygen electrodes of proton exchange membrane regenerative fuel cells. The short term chronopotentiometry test indicated good stability in the water electrolyser mode. From the polarisation curves before and after the stability test it can be seen that the MEA resistance and onset voltage did not change during the stability test. After 120 h, the degradation rate was only 0.0379 mV h⁻¹ at 22 °C. Overall this study indicates promising application of the reversible water electrolyzers in renewable power source systems such as the solar hydrogen system.

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